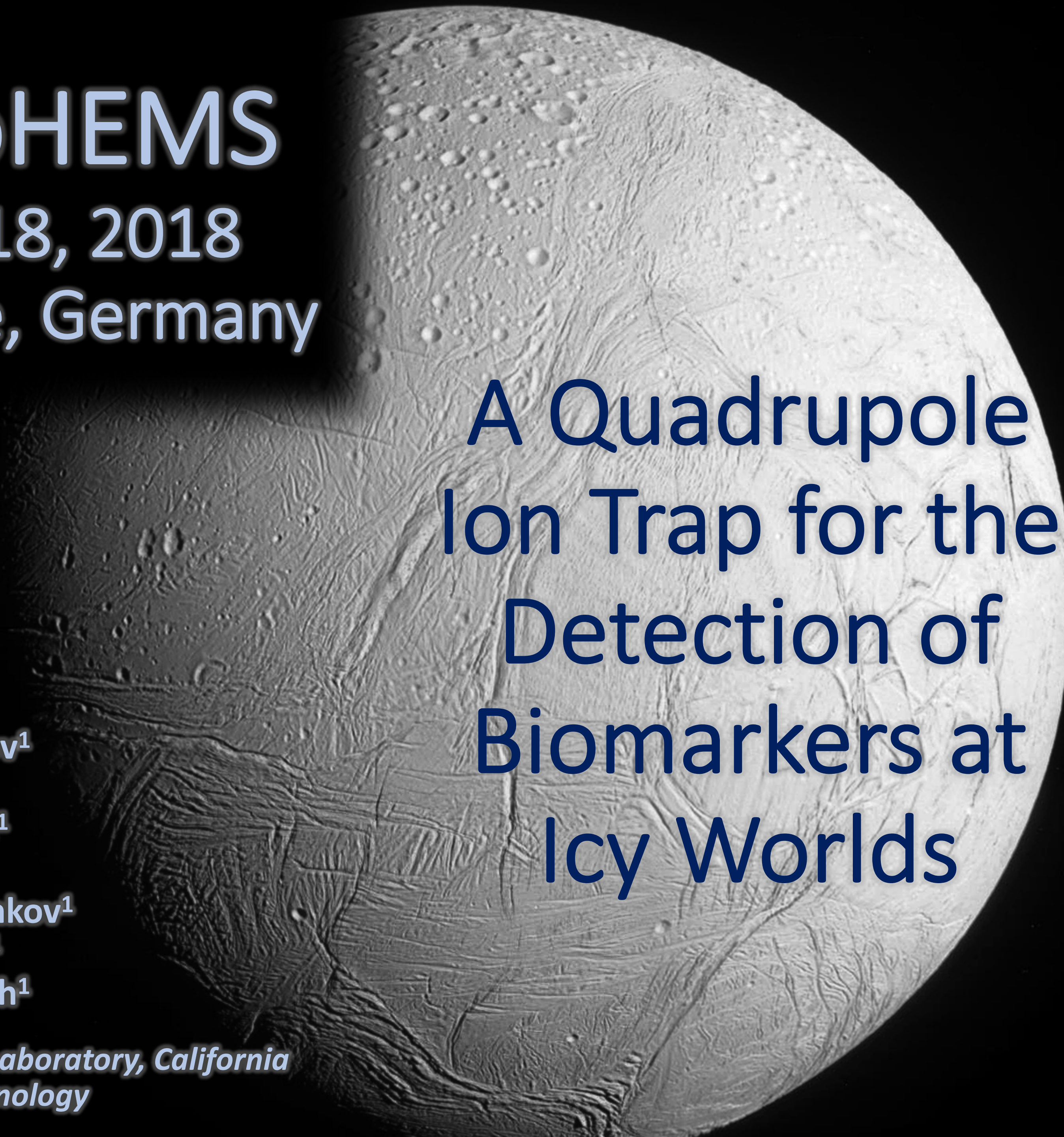

# EuroHEMS
## Oct. 18, 2018
## Cologne, Germany

# A Quadrupole Ion Trap for the Detection of Biomarkers at Icy Worlds


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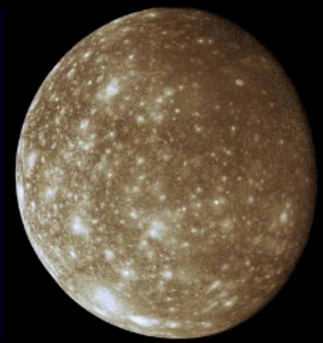
# Icy Worlds

- Ingredients for life (as we know it):
  - Water
  - Organic carbon
  - Energy source
  - Other elements: N, S, P
- 5 icy moons in our solar system that could potentially host life
- Need continued instrument development for lander and orbiter missions to search for signs of life

## Jupiter

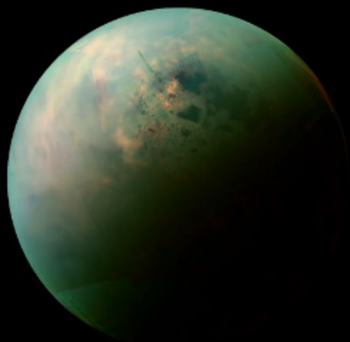
Europa



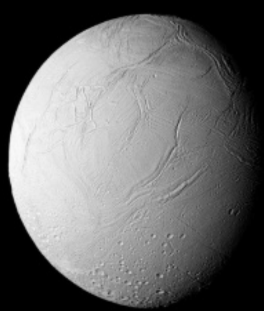
Callisto

Ganymede

## Saturn



Titan

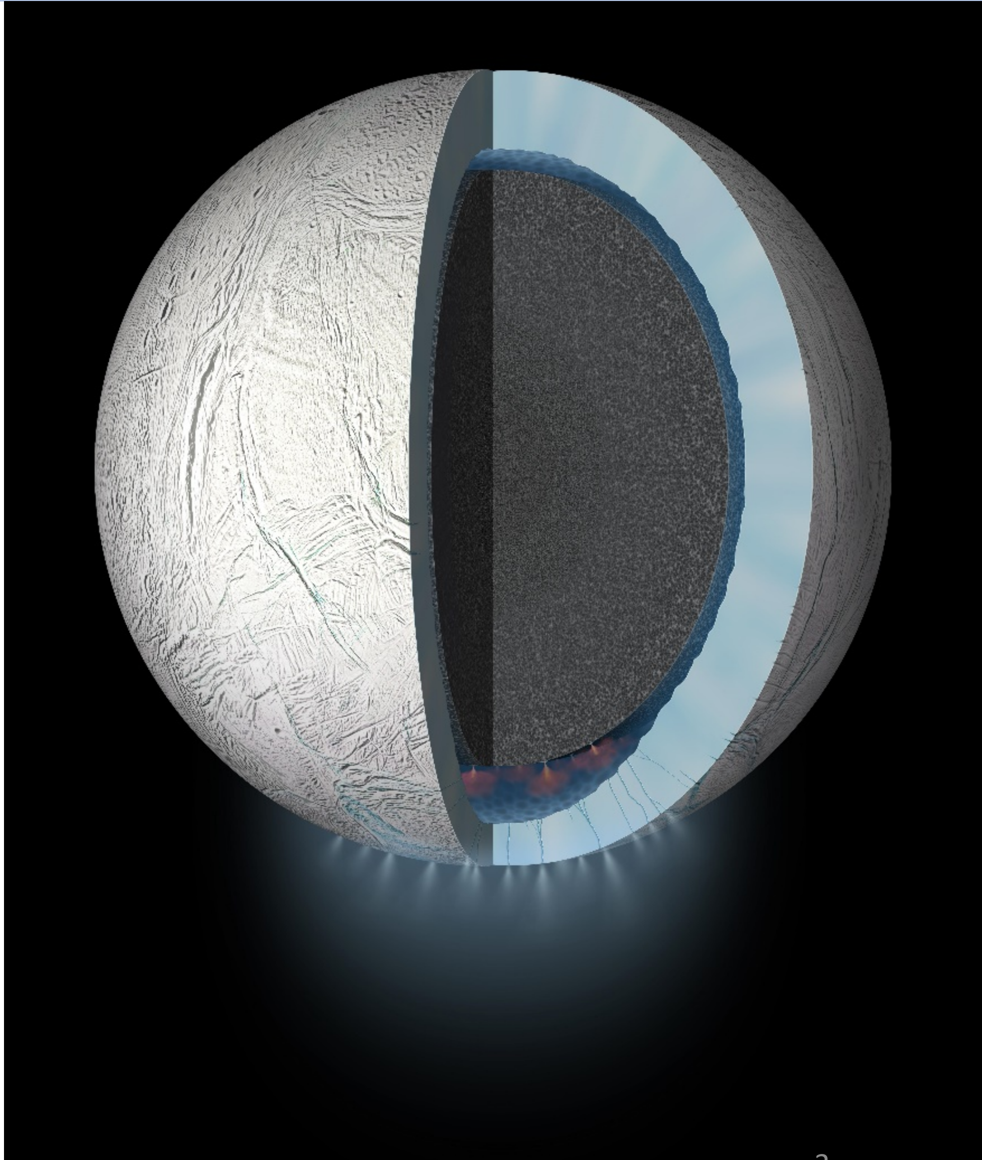


Enceladus

*Images: NASA*

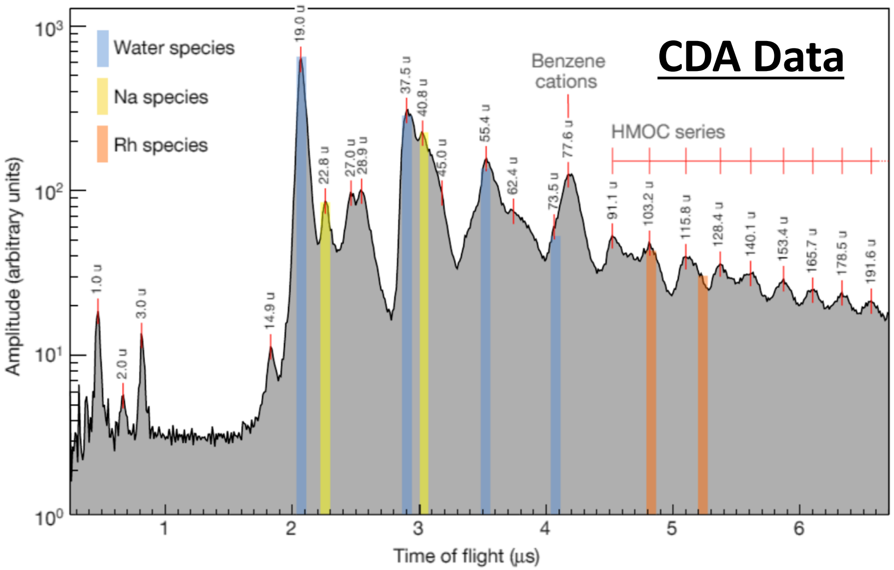
# Enceladus

- Discovered by William Herschel in 1789 (named by son John in 1847)
- 500 km diameter
- One of the most likely icy worlds to host life
- Cryovolcanoes on the south pole eject ice, water vapor, $H_2$, NaCl, etc.
    - ~200 kg of material per second
    - ~500 km from the surface
- Widely accepted to have a large, salty, and subsurface ocean
- Over 100 geysers identified
- Ice particles make up Saturn’s E-Ring

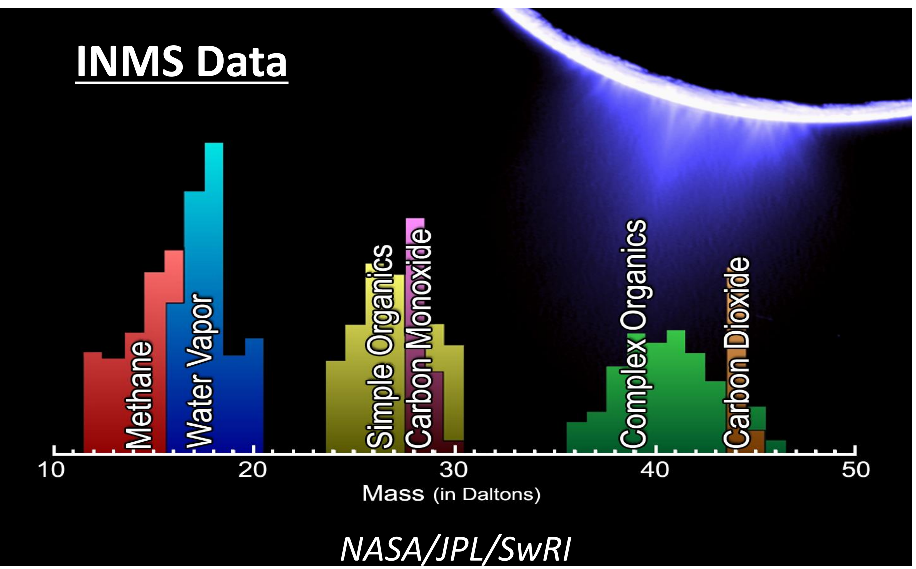


*NASA/JPL-Caltech*

# Cassini: Enceladus’ Ice Grain Analysis




Postberg, F.; *et al*. *Nature*, 558, p. 564, **2018**




Two mass analyzers were aboard Cassini

- Cosmic dust analyzer (CDA)
- Ion and Neutral Mass Spectrometer (INMS)

CDA:

- Time-of-Flight mass spectra of cations generated by high velocity (4-18 km/s) impacts of ice/dust grains on Rhodium target
- Mass range 1 – 200 Da (up to 8,000 Da)
- Mass resolution (m/Δm): 20-50

INMS:

- Detects ions and neutrals with quadrupole mass filter
- Mass range: 1 – 99 Da

Together, the CDA and INMS detected, water, salts (NaCl), benzene, methane, carbon dioxide and complex organics

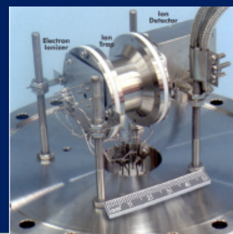
# QIT-MS Development at JPL

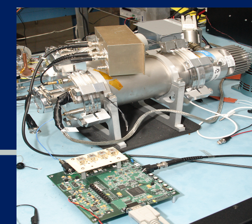
Prior, Current or Funded Flight Instrument

Recent Work

**2000**

Quadrupole Ion Trap Mass Spectrometer (QIT MS)





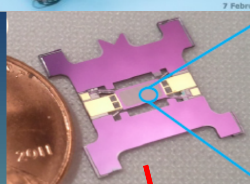
**2005**

VCAM Flight GC


Gas Chromatography (GC)

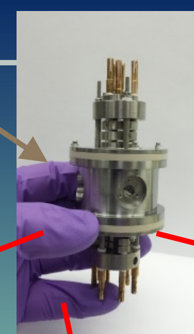
VCAM Flight QIT MS

**2010**

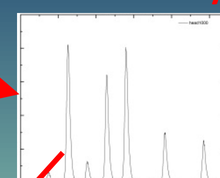


MEMS GC Development

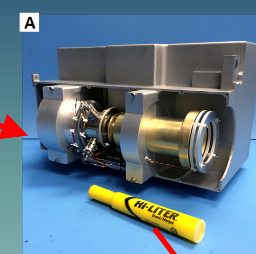
Vehicle Cabin Atmosphere Monitor (VCAM)



Noble Gas Isotopes 0.1% accuracy



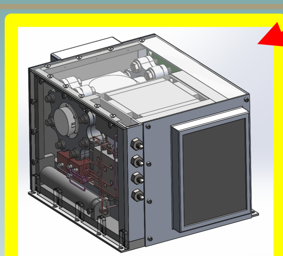
MARINE: ICCE Technology Maturation For MS




Wireless QIT MS

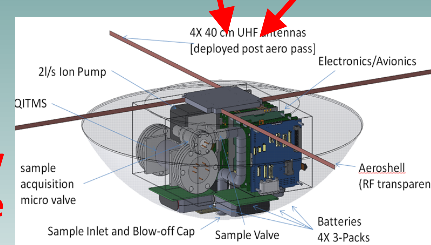
**2015**

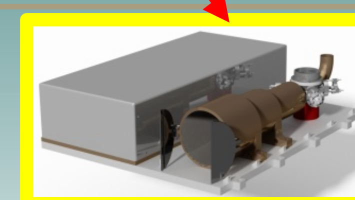
HEOMD / AES Next Generation Life Support



Spacecraft Atmosphere Monitor

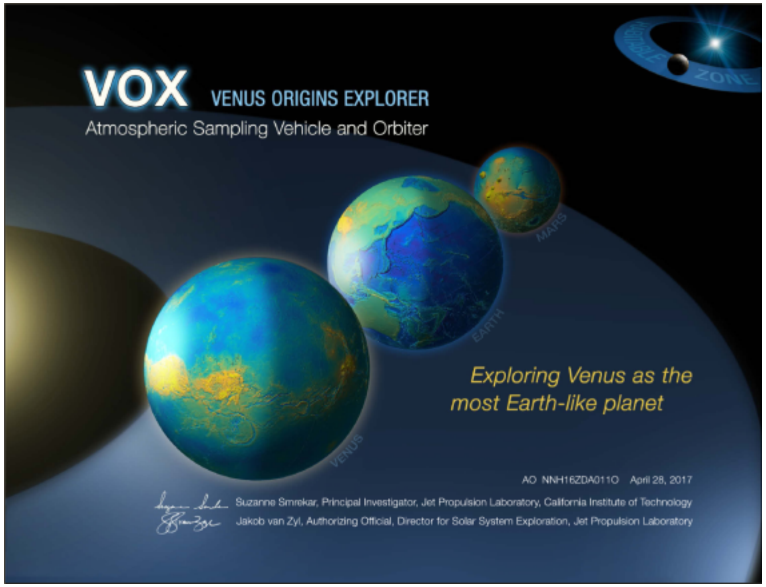
Cupid's Arrow Venus Probe



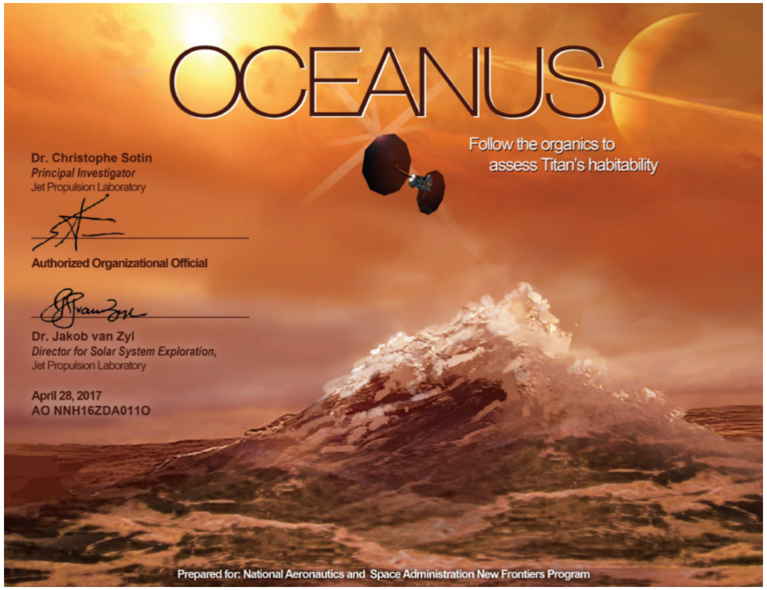



Deployment of Flyby MS on ISS

# QIT-MS on 4 New Frontiers Concepts

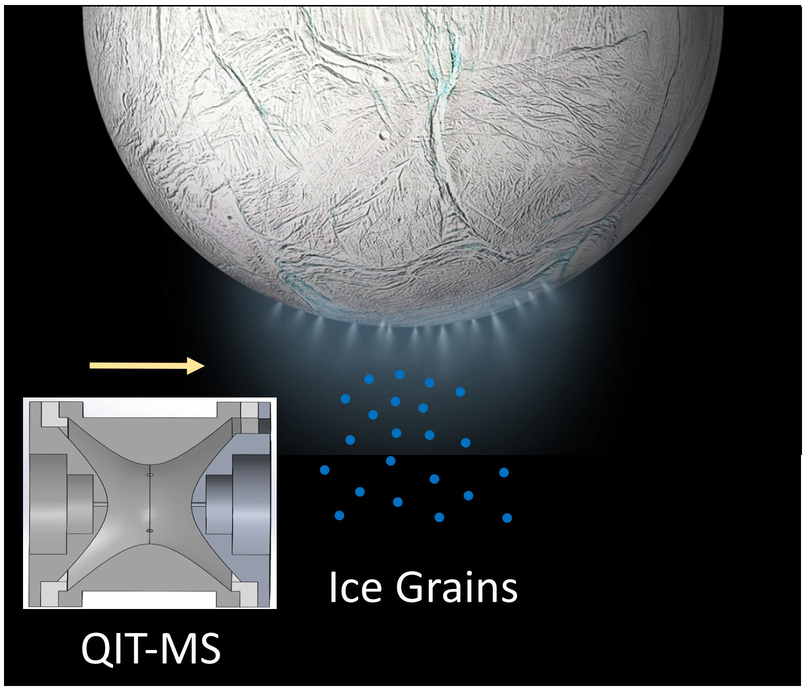







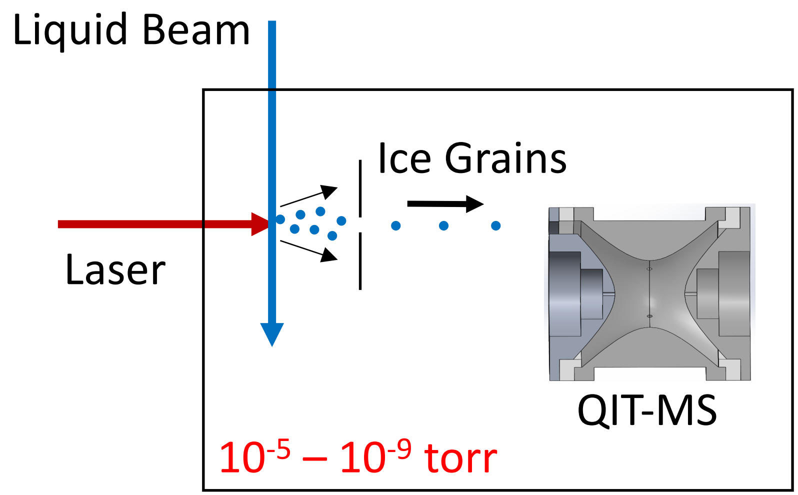
# Sampling Hypervelocity Ice with QIT-MS

**Ice Grain Sampling at Enceladus**




- QIT-MS aboard spacecraft travelling several km/s
- Ice grains from Enceladus' ocean are sampled by QIT-MS

**Ice Grain Sampling in the Lab**



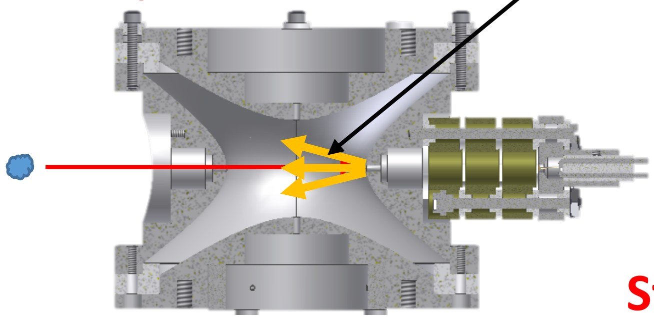

- Liquid beam formed in vacuum
- Laser impinges on liquid beam and causes shock wave-induced anisotropic dispersion of small droplets
- Small droplets travel at a few km/s into QIT-MS

**Goal: Mimic ice grain size and relative velocity in the lab**

# Internal Ionization of Neutral Species Produced by Ice Grain Volatilization

**Step 1**

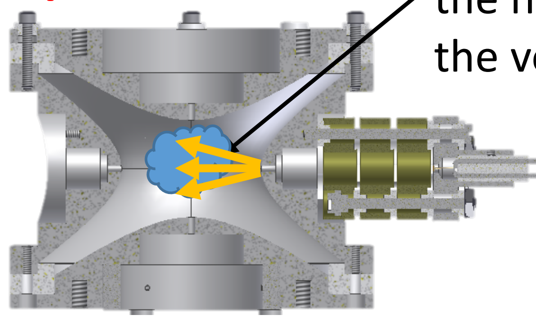
Ionizing $e^-$ beam in the QITMS



Ice grain at 5-7 km/sec enters QITMS and strikes surface causing volitization

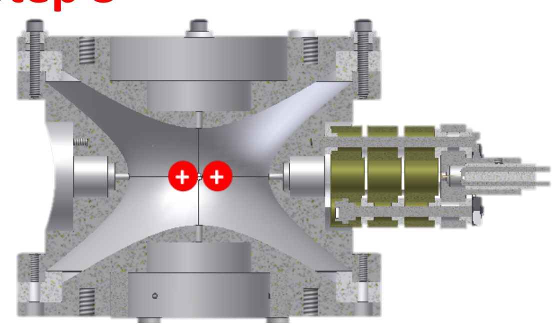
**Step 2**

$e^-$ beam or chemical ionization of the neutral gas molecules from the volatilized ice grain form ions



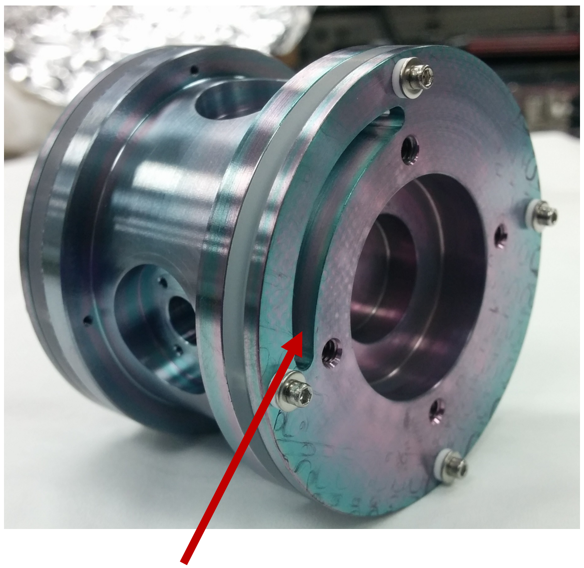
**Step 3**

Ions are mass analyzed by multi-stage mass spectrometry



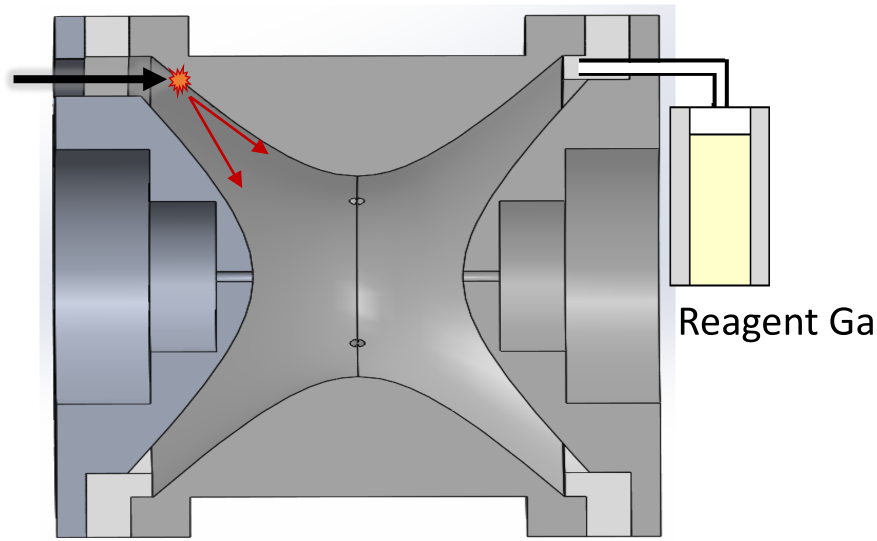
# Modifications to QIT-MS for Low Vapor Pressure Molecule Analysis

**Photo of Modified QIT-MS**



1 cm² slot for ice grains

**Solution Injection in QIT-MS Diagram**




EI – Low Pressure of R (<$10^{-5}$ torr):

CI – High Pressure of R (>$10^{-5}$ torr):

- Slot cut into QIT end cap to accept ice grains
- Trap coated with silicon-based SilcoTek coating to prevent analyte "sticking"
- Fatty/Amino solutions pumped directly into QIT-MS slot (QIT temperature: 125 ˚C)
- Adding a "reagent" allows chemical ionization (CI)
- Absence of a "reagent" results in electron ionization (EI)

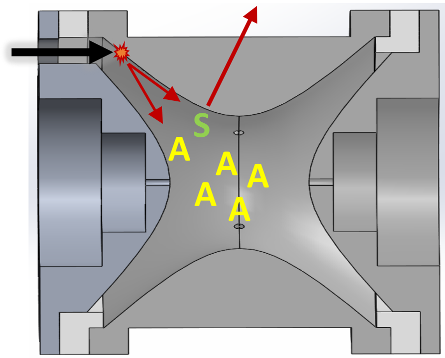
# Various Ionization Modes

## Electron Impact

- Solvent and analyte pumped into QIT
- After some time, solvent is pumped away but analyte remains
- Electron beam ionizes analyte

$$e^- + A \longrightarrow A^+ + 2e^-$$

Solvent (S) +
Analyte (A)



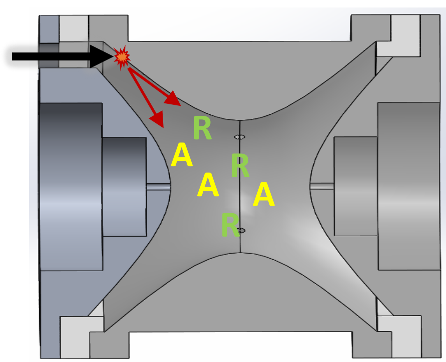

## Chemical Ionization

**Method 1:**

- Solvent and analyte continuously pumped into QIT
- Solvent is used as reagent for CI

$$RH^+ + A \longrightarrow AH^+ + R$$

Solution:
Reagent (R) +
Analyte (A)

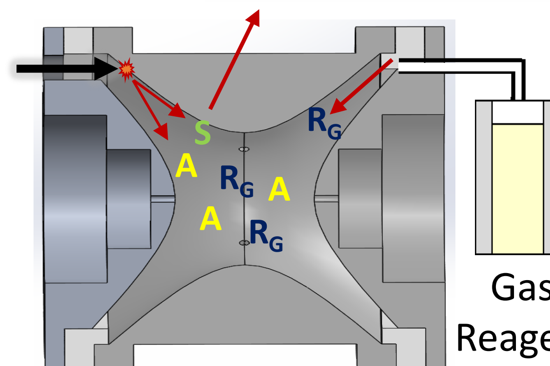



**Method 2:**

- Solvent and analyte pumped into QIT
- After some time, solvent is pumped away but analyte remains
- Reagent gas for CI added in separate port

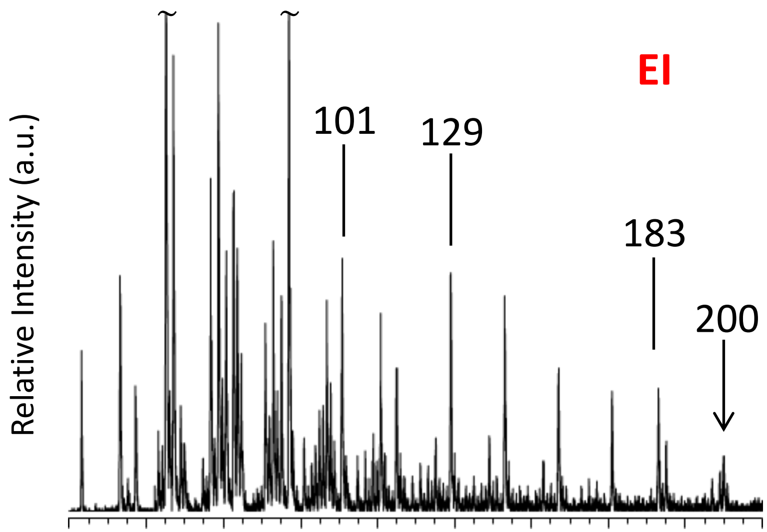
$$R_GH^+ + A \longrightarrow AH^+ + R_G$$

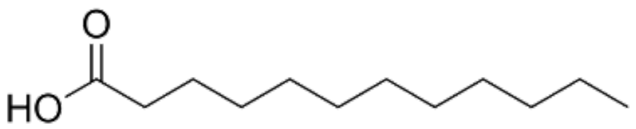
Solution:
Solvent (S) +
Analyte (A)




Gaseous
Reagent ($R_G$)

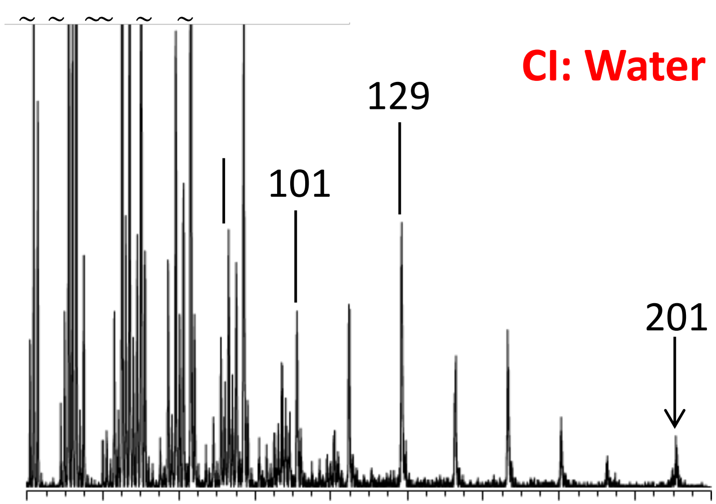
# EI vs. CI




## EI

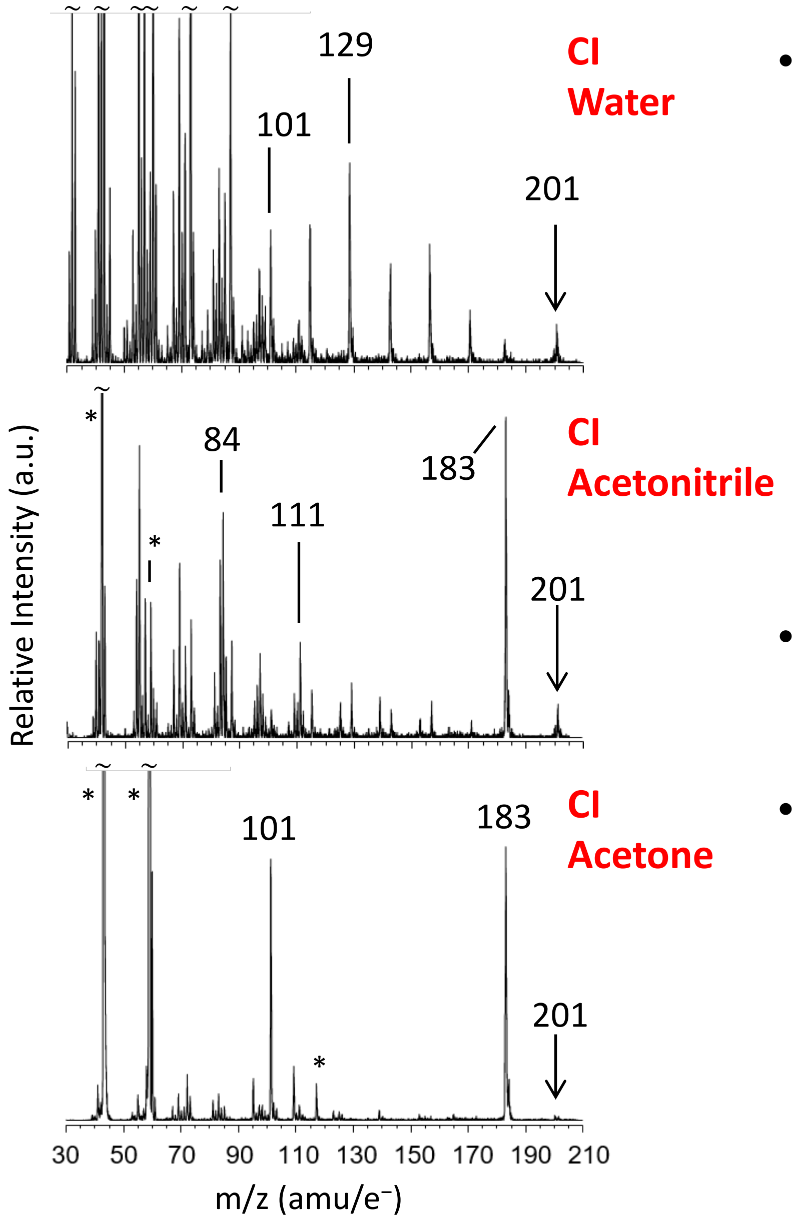
- Causes significant fragmentation ("hard")
  - Complicates mass spectra of mixtures
  - Excellent fingerprint for pure samples
- Parent peak: **Molecular cation**




## CI

- Can be "soft" or "hard" depending on reagents/samples
- CI of lauric acid with water is "hard"
  - Similar to EI spectrum
- Parent peak: **Protonated**

# "Softening" Chemical Ionization




- <u>Difference in proton affinity</u> determines extent of fragmentation

  Water > Acetonitrile > Acetone

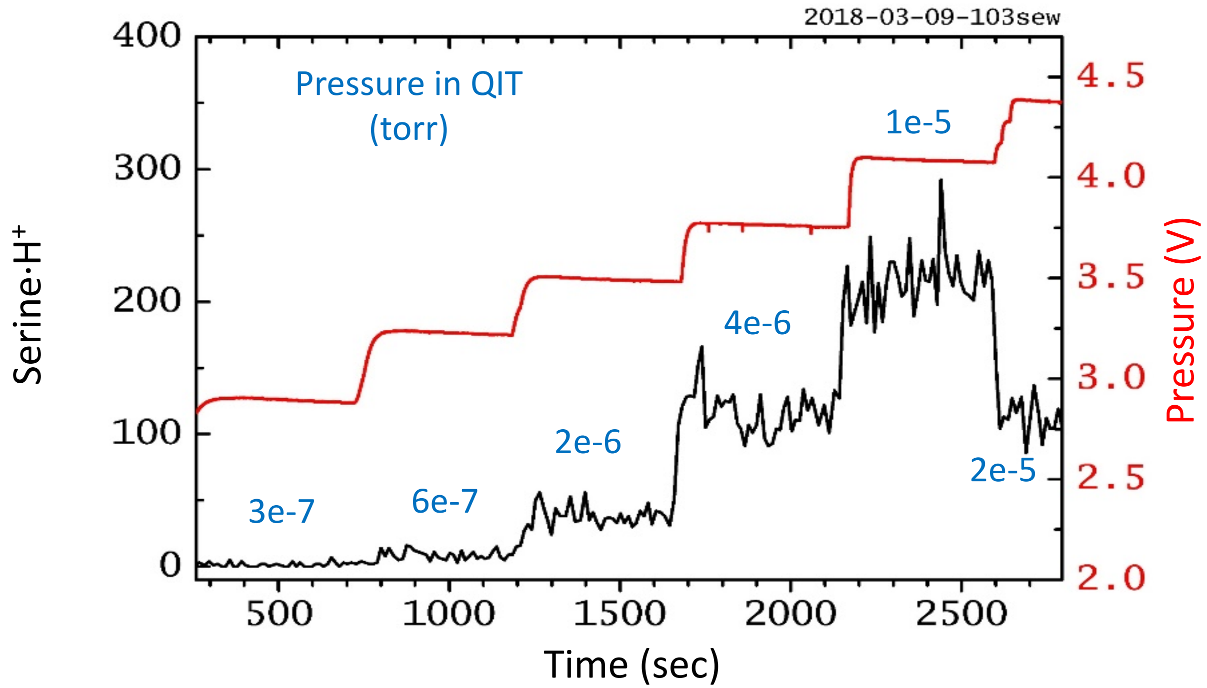
| Molecule | PA (kJ/mol) | ΔPA (kJ/mol) |
|---|---|---|
| Lauric acid | 815-825? | |
| Water | 691 | 124 (1.3 eV)* |
| Acetonitrile | 779.2 | 36 (0.4 eV)* |
| Acetone | 812 | 3 (0.03 eV)* |

** Estimated values*

- Mass spectra show less fragmentation as you work down from water to acetone

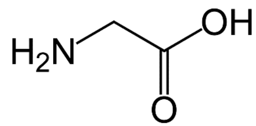
- Water CI shows more of the protonated parent ion than acetone
  - Likely due to reagent size
  - Should be able to further decrease fragmentation by using a reagent with a similar proton affinity as acetone but lower mass

# Pressure Dependence of CI



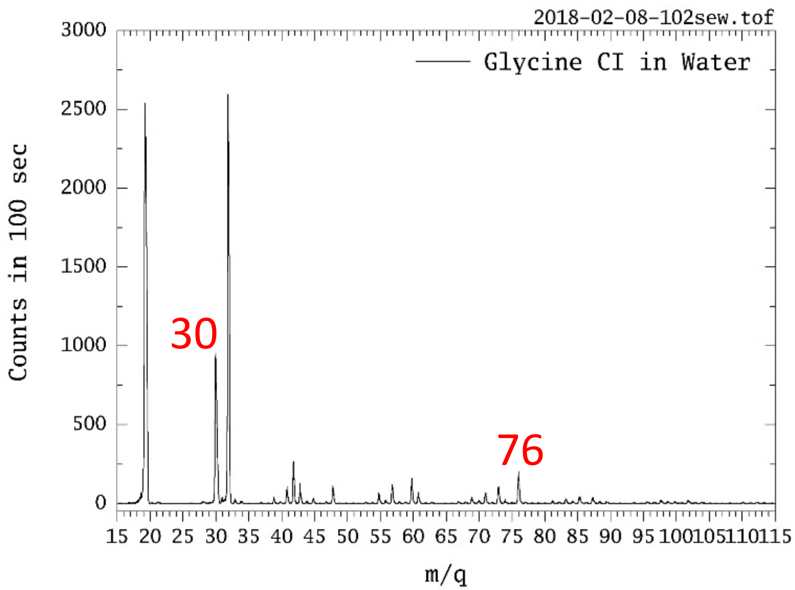

- CI is very sensitive to pressure
- Optimum CI with $1x10^{-5}$ torr acetone in QIT
- Sharp decrease in counts likely due to ion loss from collisions with acetone
    - A lighter CI reagent could possibly reduce signal loss

# Amino Acid CI in Water Mixtures

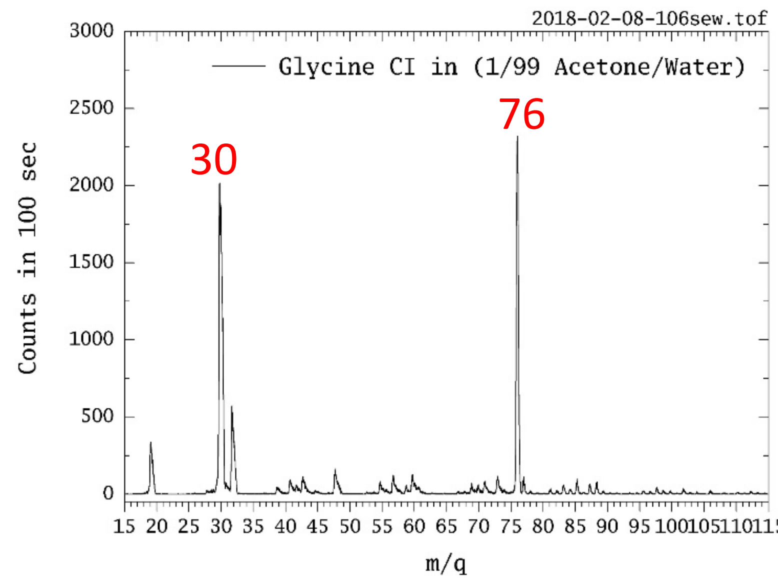



MW: 75 Da
PA: 886.5 kJ/mol

**CI: Water**




**CI: Water/Acetone (99/1)**



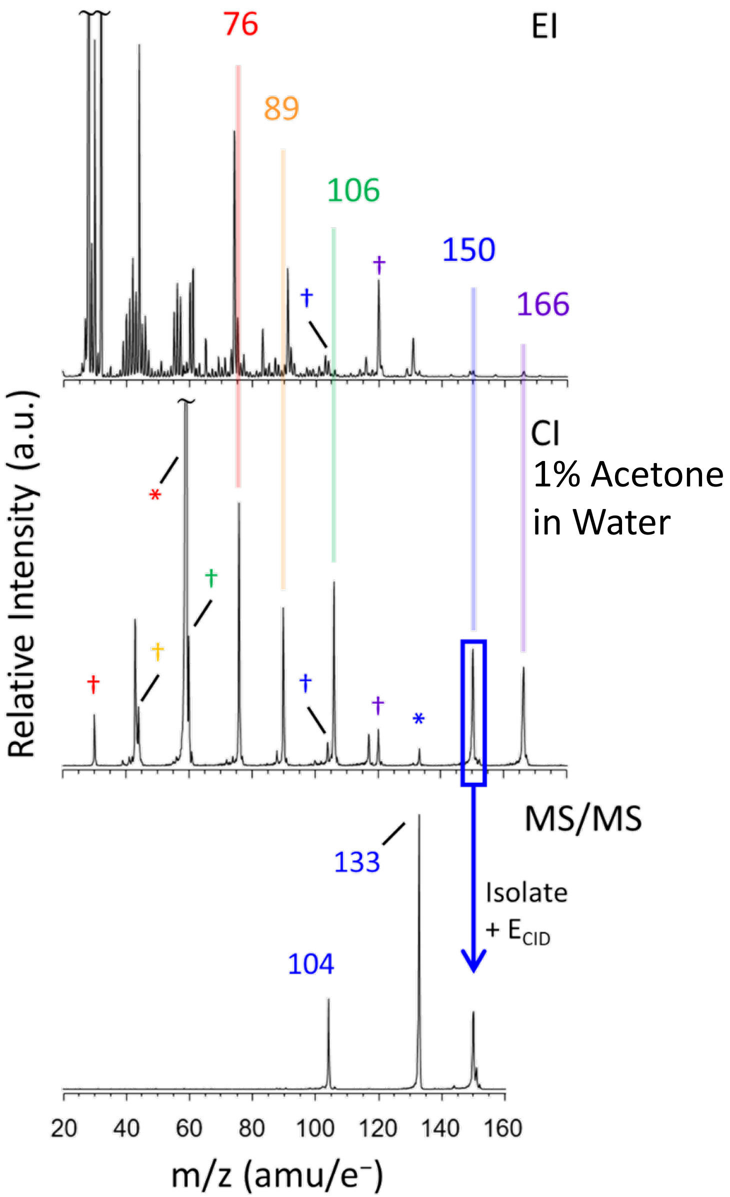

$$H_3O^+ + R_{Ac} \longrightarrow R_{Ac}H^+ + H_2O$$

$$R_{Ac}H^+ + A \longrightarrow AH^+ + R_{Ac}$$

| Molecule | Proton Affinity (PA, kJ/mol) | ΔPA w/Glycine (kJ/mol) |
|---|---|---|
| Water | 691 | 195.5 (2.0 eV) |
| Acetone | 812 | 74.5 (0.77 eV) |

- Adding acetone to a majority water background gas “softens” ionization
- A water:acetone ratio of 99:1 provides best results
  - +/- one order of magnitude also OK
- Could select separate CI reagent for softer ionization of amino acids

# Analysis of Mixtures

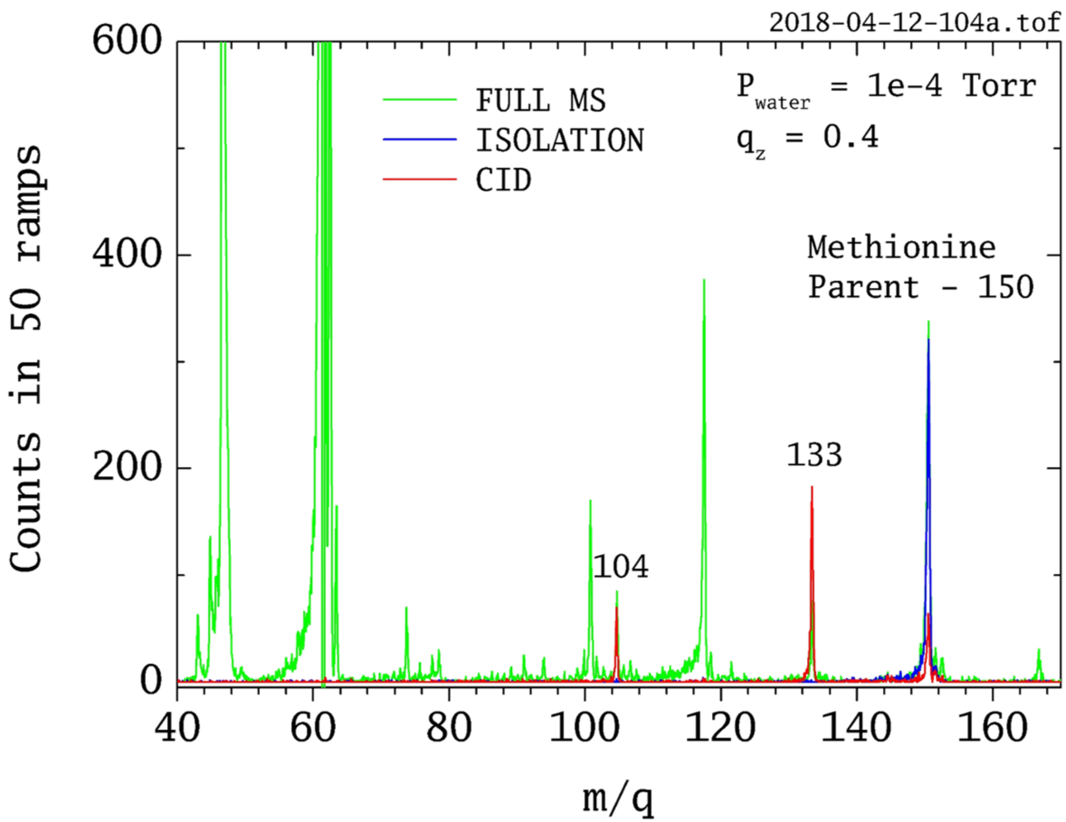



| Molecule | Mass (amu) |
|---|---|
| Glycine | 75 |
| Alanine | 88 |
| Serine | 105 |
| Methionine | 149 |
| Phenylalanine | 165 |

- EI mass spectrum quickly becomes congested with fragment peaks (esp. *m/z* 30 – 100)
- Can differentiate all 5 parent ions
  - Some fragmentation
- Can perform MS/MS for further structural confirmation

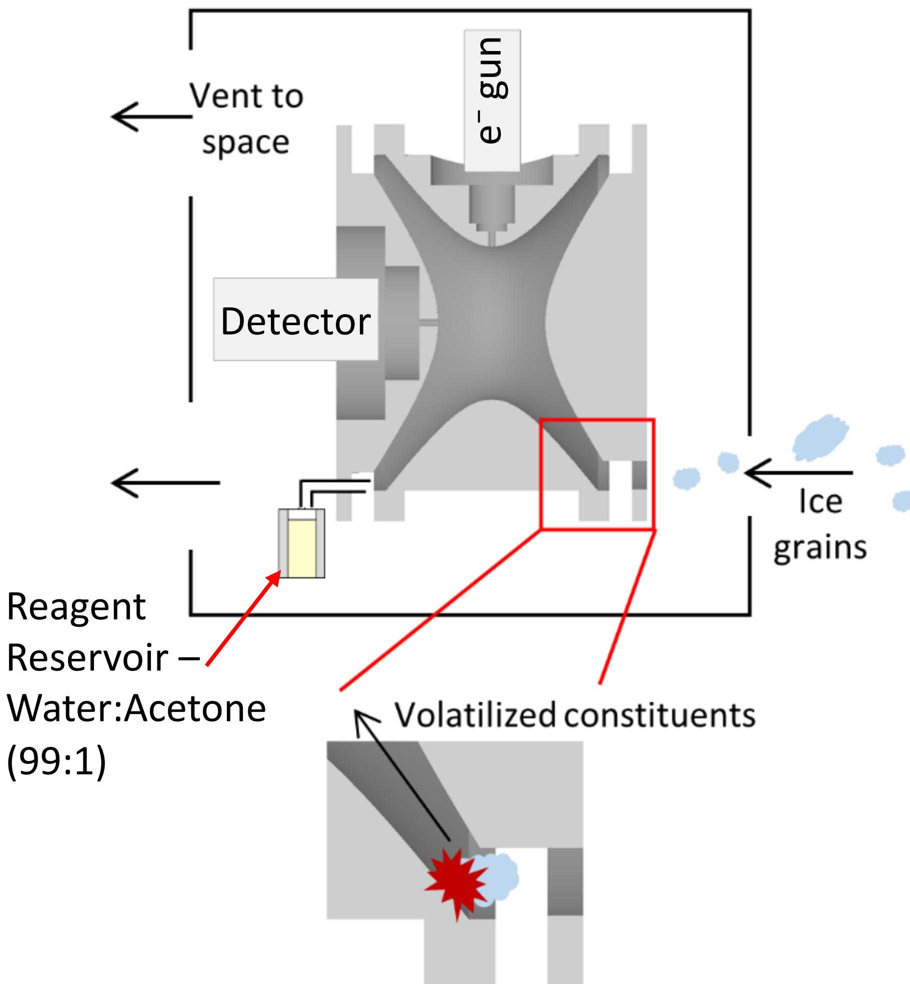
# MS/MS with Water Collision Gas

## CID agent: Water (with 1% Acetone)




- Minimal losses during isolation
- ~50-70% fragmentation efficiency
- Fragments at 133 and 104 amu
  133: Ammonia loss
  104: Formic acid loss
- Works well for all of the amino acids so far
  - Having some issues with fatty acids (lose water before activation)

# Design for Hypervelocity Ice Sampling



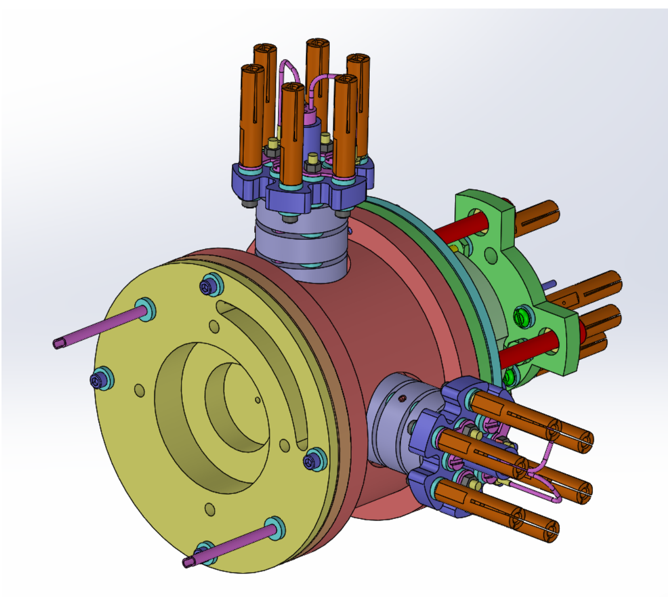

- Space venting to save space and power consumption
- Introducing water vapor with the acetone CI reagent vapor should help mitigate the effects of pressure fluctuations
- Potentially send two CI reagents
  - One for fatty & amino acids
  - One for amino acids

| Molecule | PA (kJ/mol) |
|---|---|
| Lauric acid | 815-825? |
| Glycine | 886.5 |
| Acetone | 812 |
| Ammonia | 853.6 |
| Chloromethylene | 874.1 |

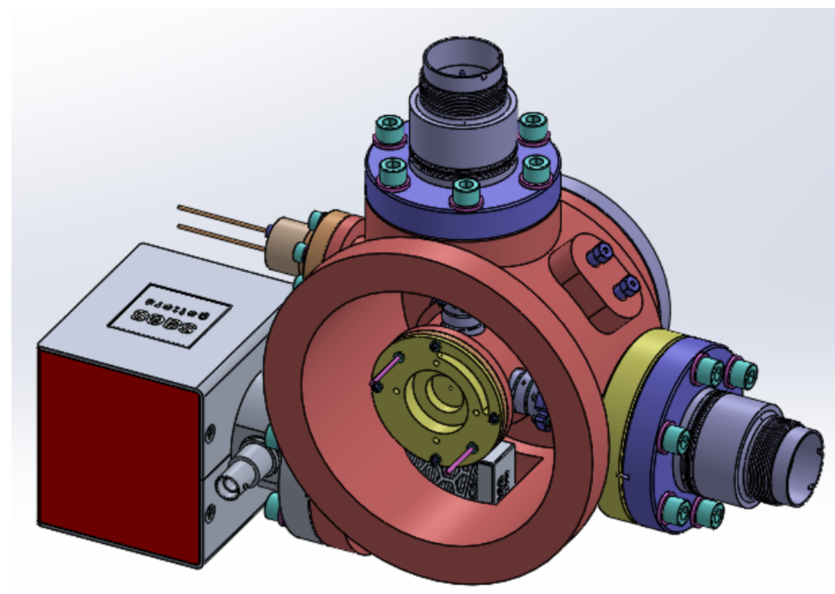
# Next Steps

- MS/MS to identify potential confounding isomers in a mixture


- Interface with hypervelocity ice gun

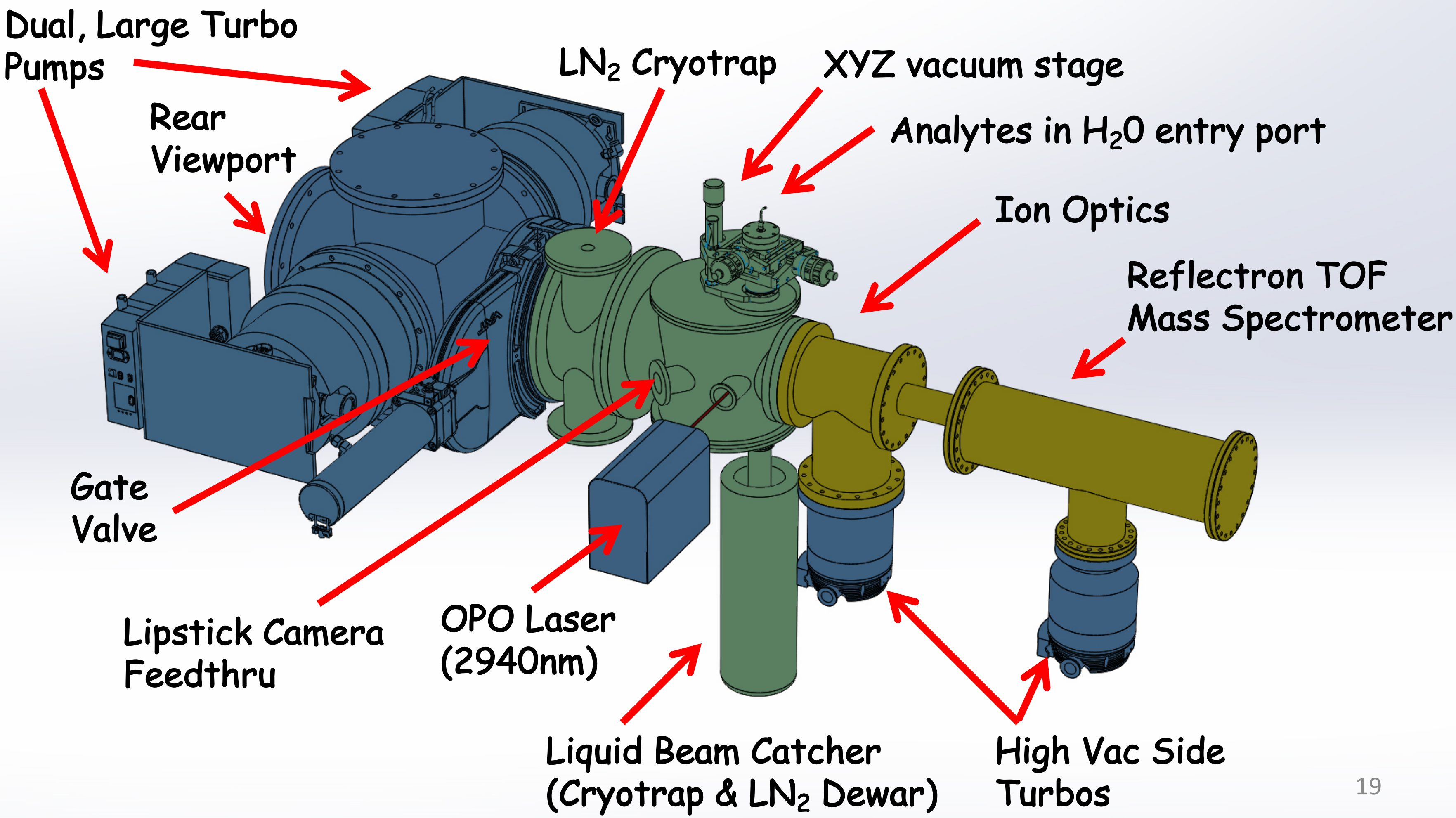


*Side-ionization-capable QITMS with hypervelocity input and gas delivery*



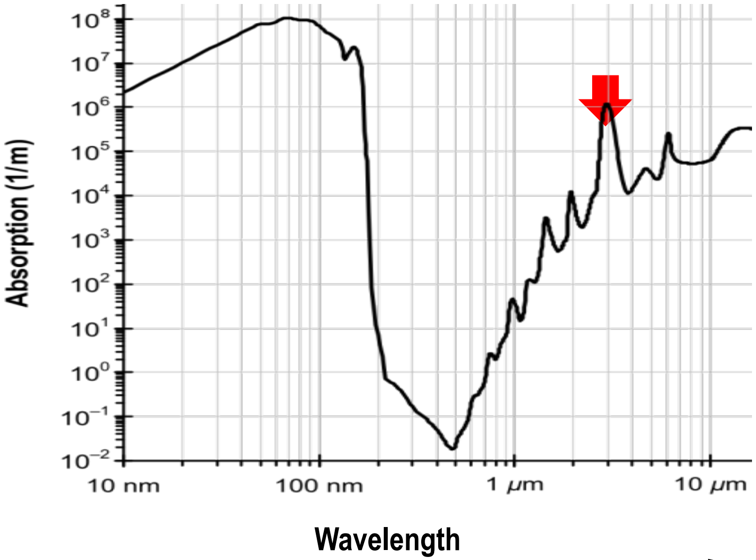
*Enclosure optimization for interface to hypervelocity ice gun.*

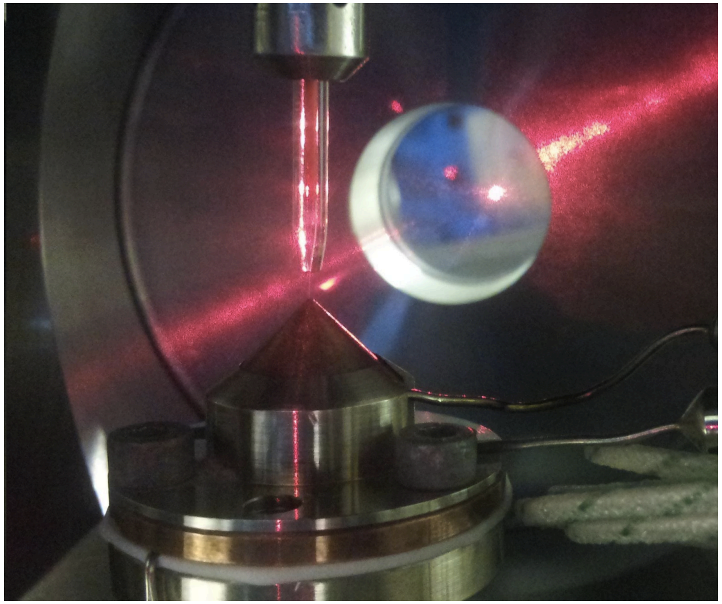
# Hypervelocity Ice Gun

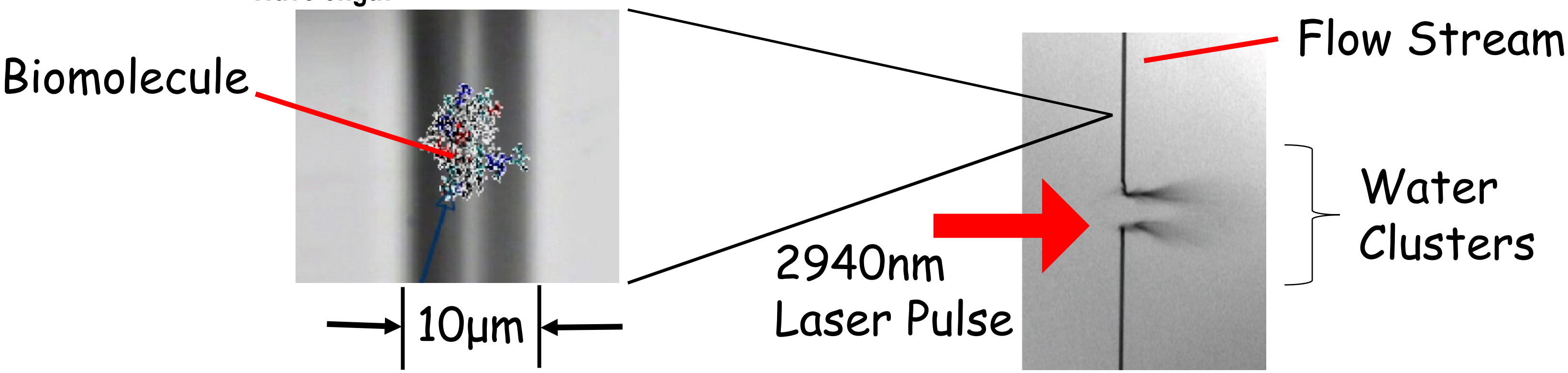


# Generating Hypervelocity Ice Grains in the Lab

Absorption Spectrum of Water






IR Laser/Liquid Beam Interactions in the testbed generate neutral and charged particles with mass and velocity distributions analogous to the Enceladus Ice plume/QTIMS interactions.

# Conclusions

- Soft chemical ionization of amino/fatty acids was achieved in the QIT-MS in water-rich environments like those expected when sampling ice grains at hypervelocity

- A mixture of water:acetone (99:1) is capable of relatively soft ionization of both amino and fatty acids
  - Will continue to search for a lighter reagent with similar proton affinity as acetone
  - Could use a separate reagent for CI of amino acids with reduced fragmentation
  - Effective for mixtures

- The water/acetone mixture has been successfully used as a collision gas for MS/MS

# Acknowledgements


- Frank Postberg – Hypervelocity Ice Gun - Heidelberg

- Bernd Abel – Hypervelocity Ice Gun - Leipzig

- Other JPL team members:
  - All other authors, especially **Sarah Waller** and **Anton Belousov**
  - Jurij Simcic – Engineering/Design
  - Rembrandt Schaefer – RF Electronics
  - James Lambert – Hypervelocity ice (JPL)
  - Nick Tallarida – Hypervelocity ice (JPL)
  - Rob Hartsock – Hypervelocity ice (JPL)